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57 Sheet-like, multilayer, laser-optical recording material, with

- a) an optically transparent and isotropic, homogeneous substrate free from orientation birefringence

and

- b) at least one amorphous, thermally modifiable recording layer, wherein the substrate (a)

a₁) has one or two structured surfaces, wherein the structures are in the micrometer and/or submicrometer range,

and is formed from a blend of Poly(2,6-dimethylphenylene ether) (PPE) with at least one styrene polymer, where the content of PPE in this blend is approximately 25 to 45 % by weight, based on the blend, and wherein

a₂) that part of the blend without PPE contains, based on this part,

a₂₁) 0.1 to 8 % by weight of cyanoethylene groups and/or

a₂₂) 1 to 60 % by weight of 1-methyl-1-phenylethylene groups and/or

a₂₃) 1 to 60 % by weight of 4'-methyl phenyl-ethylene groups and/or

a₂₄) 0.01 to 10 % by weight of groups of the general formula I

in which R^1 indicates a hydrogen atom or a methyl radical and R^2 a C_1 - to C_{10} -alkyl-, C_5 - to C_8 -cycloalkyl- or a C_6 - to C_{10} -aryl radical,

and

a₂₅) contains at least 40 % by weight of phenylethylene groups

Further those audio or video compact disks are claimed, which contain a substrate formed accordingly.

Sheet-like, multilayer, laser-optical recording material

The invention concerns a new sheet-like, multilayer, laser-optical recording material that has improved performance characteristics with

a) one or more layers of an optically transparent and isotropic, homogeneous blend of poly(2,6-dimethyl phenylene ether) (PPE) free from orientation birefringence with styrene polymer as substrate and

b) at least one amorphous, thermally modifiable recording layer.

Recording materials of this type are known, for example, from the US-A-4 373 065 or EP-A-225 801.

In the scope of this invention the term "sheet-like" covers all 3-dimensional forms, with thickness that is considerably less than the length and the width. Accordingly, here it may concern recording materials in the form tape, plate or disk, where the disk-like recording materials are also generally called data disks or simply disks.

The term "amorphous" indicates that the material of the recording layers (b) has no crystalline regions, which are larger than the thermally modified regions, but that it is optically isotropic in this order of magnitude.

In the recording layers (b) of recording materials of the type under discussion, digital data are written with the help of pulse-modulated write laser beams in the form of

thermally modified regions. The write laser beams are focused on the recording layers (b) and/or strike them perpendicularly. For writing analog data, continuous wave lasers can also be employed. In the case of written digital data the thermally modified regions of the recording layers (b) have a circular or elliptical base area. In the case of analog data the thermally modified regions can have any base area.

For the reading of the data, in general, continuously emitted read laser beams (continuous-wave laser beams) are used, whose energy is not adequate to produce further changes in the recording layers (b). The read laser beams are also focused on the recording layers (b) and/or strike them perpendicularly. Generally during the reading process the light reflected by the recording layers (b) is collected with the help of suitable optical arrangements, fed to conventionally known detectors and converted into signals by suitable electronic equipment.

This write and read process as well as the corresponding suitable recording materials are therefore identified with the term "laser-optical", wherein generally the write and read process is subsumed by the term "data recording".

Therein the thermally modified regions of the recording layers (b) may have the form of holes, which penetrate the recording layer completely. In this case the term ablative laser-optical data recording is usually used. While reading the data with a read laser beam, the varying reflectivity of the holes and the unchanged regions of the recording layer (b) are utilised. In order to obtain high sensitivity and a high signal-to-

noise ratio, it is also possible to use a reflector layer that is exposed by the hole formation and reflects the read laser beam quite intensely.

The thermally modified regions can also be in the form of pits that, in certain cases, can have a cleanly formed wall (edge). In this case, the term deformative laser-optical data recording is used. Here, the data is read by means of the diffraction of light of the read laser beam at the craters.

However, the thermal change can also result in regions undergoing no ablation or deformation, but a phase transformation of the material of the recording layer into another material modification. In such a case the term used is laser-optical data recording by phase transformation. Usually, the reflectivity is reduced in the described regions by the phase transformation and/or the light transmittance is increased. However, under certain conditions, it may also have the opposite effect, i.e., the reflectivity is increased and/or light transmittance is reduced. The regions thermally modified in this manner are called spots.

The recording layers (b) can however be underlaid with layers, which expand during the exposure or produce gases, by which the recording layers (b) are expanded locally. In this manner, relief structures that contain the recorded data are formed on the surface of the recording layers (b).

The gases can be released in the recording layers (b) themselves with the formation of small light-scattering bubbles. This is called vesicular data recording.

In addition, in the thermally modified regions a chemical reaction of one component or a chemical reaction among several components of the recording layers (b) may have taken place, leading to a change in the optical properties of the recording layers (b) in these regions. During exposure a local change in the reflectance of the recording layers (b) can also happen through enlargement or fusion of small particles. These small particles, for example, gold granules, can be deposited in a matrix. It may involve plastic spheres coated with metal by vapour deposition. Recording layers (b), consisting of these spheres, have extremely low basic reflectivity and are generally called "moth eye layers".

Furthermore, the thermally modified regions in recording layers (b), which consist of magnetised, amorphous, ferrimagnetic layers at right angles to their surface, may have the form of spots, which have a magnetisation direction opposite to the original direction. These "spots" are formed during heating of the ferrimagnetic material of these layers by a laser beam under the influence of an adjacent auxiliary magnetic field: Heating increases the coercive field strength H_c of the ferrimagnetic material. If the coercive field strength H_c falls below the field strength of the adjacent auxiliary magnetic field at a critical temperature dependent on the material used at a given time, then that region undergoes magnetic reversal.

For reading these regions, linearly polarised light of a continuously emitting continuous-wave laser, whose light output is not sufficient to heat the material beyond the critical temperature, is used. This laser beam is reflected either by the recording layer (b) itself or by a reflector layer arranged behind it, resulting in an interaction between the magnetic moments in the recording layer (b) and the magnetic vector of the laser light wave. Due to this interaction, the plane of polarisation \vec{E} of the laser light, which is reflected by a "spot" or by a reflector layer behind it, is rotated by a small angle with respect to the original plane. If this rotation of the plane of polarisation \vec{E} takes place during the reflection of the light at the recording layer (b) itself, then this is called the Kerr effect and the corresponding angle of rotation is called the Kerr angle of rotation. If, on the other hand, the plane is rotated during the two-time passage of the light through the recording layer, then the terms Faraday's effect and Faraday angle of rotation are used.

This rotation of the plane of polarisation \vec{E} of the laser light reflected by the recording material can be measured with the help of suitable optical and electronic equipment and converted into signals.

Recording layers (b) of this type are identified by the term "magneto-optical".

In the case of multilayer, laser-optical data disks and also in the case of known audio and video compact disks, the conventionally known disk drives are generally used for writing and/or reading digital data. Such a disk drive contains essentially a disk turntable and a laser-optical write and read head, as well as mechanical servo systems for the correction of the track position, auto-focusing means, optical elements for the analysis of track position and auto-focus errors, detector devices with upstream optical

components for the recording of the light of the read laser beam reflected by the data disks as well as suitable electronic components. Usually a laser-optical write and read head contains laser diodes that emit infrared light and consist of semiconductor materials such as GaAlAs. Moreover, such a write and read head has some more related optical components, such as dielectric beam dividers, polarisation beam dividers or polarisation-independent beam dividers as well as a $\lambda/4$ or $\lambda/2$ -plate.

The laser-optical recording materials used currently contain a dimensionally stable substrate that is an optically transparent disk of plastic or a plastic blend having thickness of 1.2 mm and diameter of 83 to 350 mm, in the case of laser-optical data disks or the known audio and video compact disks. Here, plastics are typically: polycarbonate, polymethyl methacrylate, polymethyl pentene, cellulose acetobutyrate or blends of poly(vinylidene fluoride) and polymethyl methacrylate. Substrate of this type, however, have serious disadvantages, such as a optical orientation coefficient (orientation birefringence) that is too high, very high processing temperature, very low heat distortion resistance, very low modulus of elasticity, very low hardness or very high water absorption. Depending on the plastic or plastic blend used, these disadvantages are more or less in number; none of the known materials have an optimum property profile.

However, if the dimensionally stable substrate corresponds to a layer (a) of the laser-optical recording material given in the US-A-4 373 065, then many of the mentioned disadvantages do not exist any more. Such a layer (a), which consists of poly(2,6-dimethyl phenylene ether) (PPE) and polystyrene, is optically transparent and

isotropic, homogeneous, free of orientation birefringence, resistant to heat distortion and mechanically stable. Moreover its water absorption is low. This property profile of the layer (a) is preserved throughout its use as a substrate.

Nevertheless these substrates have disadvantages that prevent them from being used in practice. Then the processing temperature of the known polystyrene/PPE blends is undesirably high due to their poor flow property. If an attempt is made to eliminate this characteristic by lowering the PPE content and/or by lowering the molecular weight of the polystyrene, then further disadvantages such as, for example, increased orientation birefringence, a decreased modulus of elasticity or poor solvent resistance, are encountered. Laser-optical recording materials that contain such substrates have often intensely varying signal-to-noise ratio with the same type of recording layer (b). In addition, in a frequent and unpredictable manner, the recovery of recorded data becomes difficult, i.e., the tracking behaviour of such recording materials is not very satisfactory and not sufficient in practice, where rapid access to the data is essential. Also, with substrate materials of PPE/polystyrene blends known from EP-A-225 801, which should have a relatively low molecular weight PPE for reducing the processing temperature, these disadvantages are not completely removed and the existing problems have not yet been solved fully satisfactorily.

The task of the present invention is to find a new, sheet-like, laser-optical recording material, which does not have the disadvantages of the present technology.

Correspondingly a new, sheet-like, multilayer, laser-optical recording material was found with

a) one or more layers of an optically transparent and isotropic, homogeneous blend of poly(2,6-dimethylphenylene ether) (PPE), free from orientation birefringence, with a styrene polymer as substrate and

b) at least one amorphous, thermally modifiable recording layer, which is characterised by the fact, that the layer (a) forming a dimensionally stable substrate

a₁) has one or two structured surfaces in which the structures are in the micron and/or sub-micron range,

and is formed from such a PPE blend, containing at least one styrene polymer as well as in certain cases additives, in which the content of PPE is in the range of 25 to 45 % by weight, based on the blend, and in which

a₂) that part of the blend not having PPE contains, based on this part (a₂),

a₂₁) 0.1 to 8 % by weight of cyanoethylene groups and/or

a₂₂) 1 to 60 % by weight of 1-methyl-1-phenyl-ethylene groups and/or

a₂₃) 1 to 60 % by weight of 4'-methylphenyl-ethylene groups and/or

a₂₄) 0.01 to 10 % by weight of groups of the general formula 1

in which R^1 indicates a hydrogen atom or a methyl radical and R^2 a C_1 - to C_{10} -alkyl, C_5 - to C_8 -cycloalkyl or a C_6 - to C_{10} -alkyl radical, with the proviso, that

a₂₅) Regardless of whether one or more of the groups (a₂₁) to (a₂₄) and in certain cases some additives are present in (a₂), the part (a₂) that, in any case, contains phenylethylene groups not less than 40 % by weight.

An essential component of the recording material related to the invention is the layer (a) that forms the dimensionally stable substrate, which is called hereinafter as "substrate (a) to be used according to the invention" or simply "substrate (a)".

The substrate (a) according to the invention has one or two structured surface(s) (a₁). These surfaces (a₁) are turned towards the recording layer(s) (b). Substrates (a), which have only one structured surface (a₁), are preferred.

The structures on the surface (a₁) are in the micron and/or sub-micron range. They serve to guide the read laser beam, ensuring rapid and exact response of the tracking servo and auto-focusing means in the laser-optical write and read heads of the disk drives, i.e., they enable or improve tracking. In addition, these structures themselves can contain or represent data, as is the case, for example, in the known audio or video compact disks, or they can serve for the coding of recorded data. In practice, the structures consist of raised parts and/or indentations. These are present in the form of continuous concentric or spiral tracks or isolated hills and/or holes. In addition the structure may have a more-or-less smooth waveform. The tracks are preferred here. They

have right-angled sawtooth-like, V-shaped or trapezoidal contour in the transverse direction. The indentations are called "grooves" and the raised parts, "land". Tracks with 50 to 200 nm deep, 0.4 to 0.8 μm wide "grooves", with 1 to 3 μm wide "land" between, are particularly advantageous.

The blend, which forms the substrate (a) according to the present invention, contains from 25 to 45 % by weight, preferably 32 to 42 % by weight and in particular 4 to 40 % by weight, of poly(2,6-dimethylphenylene ether) (PPE). The intrinsic viscosity of the PPE in general is in the 0.5-0.8 dl/g range, preferably in the 0.5 to 0.7 dl/g range (measured at 25° C in chloroform). The processes for the preparation of PPE are given in EP-A-0 161 454.

In addition, this blend contains a part (a_2) not containing PPE. This part (a_2) constitutes 55 to 75 % by weight, preferably 58 to 68 % by weight and in particular 60 to 68 % by weight of the blend.

Particularly suitable blends for the formation of the substrate (a) consist of 34 to 40 % by weight PPE and 60 to 66 % by weight of the part (a_2).

According to the present invention, the part (a_2) contains polymers that have copolymerised styrene as an essential component, or the part (a_2) essentially consists of polystyrene. Here "essentially" means copolymerised styrene content in the polymers of the part (a_2) of more than 40 % by weight, what is equivalent to a content of more than 40 % by weight of phenylethylene groups. This content should not fall below 40 % by weight, because otherwise it may cause a certain separation of the part (a_2) and the PPE in the course of time, what will lead ultimately to opacity of the substrate (a) and make it useless.

According to the present invention the part (a₂) of the blend of PPE and (a₂) contains groups (a₂₁), (a₂₂), (a₂₃) and/or (a₂₄), which can be used individually or together. Regardless of whether one or more of these groups (a₂₁) to (a₂₄) are used, the content of (a₂₅) phenylethylene groups in (a₂) does not fall below 40 % by weight; at the most it is equal to 40 % by weight.

Accordingly, the part (a₂) of the blend that is formed by the substrate (a) to be used, according to the present invention, may consist of the following combinations of groups or contain these combinations of groups:

phenylethylene + (a₂₁),

phenylethylene + (a₂₁) + (a₂₂),

phenylethylene + (a₂₁) + (a₂₃),

phenylethylene + (a₂₁) + (a₂₄)

phenylethylene + (a₂₁) + (a₂₂) + (a₂₃),

phenylethylene + (a₂₁) + (a₂₂) + (a₂₄),

phenylethylene + (a₂₁) + (a₂₃) + (a₂₄),

phenylethylene + (a₂₁) + (a₂₂) + (a₂₃) + (a₂₄)

phenylethylene + (a₂₂),

phenylethylene + (a₂₂) + (a₂₃),

phenylethylene + (a₂₂) + (a₂₄),

phenylethylene + (a₂₂) + (a₂₃) + (a₂₄),

phenylethylene + (a₂₃),

phenylethylene + (a₂₃) + (a₂₄) and

phenylethylene + (a₂₄).

Here the combinations of the phenylethylene groups (a₂₅) and the groups (a₂₁), (a₂₂), (a₂₃) or (a₂₄) as well as the combinations of the phenylethylene groups (a₂₅) and the groups (a₂₂) and (a₂₃) are particularly advantageous.

Of these again the combination of the phenylethylene groups (a₂₅) and the groups (a₂₂) and (a₂₃) is most preferred.

In the case of the group (a₂₁) it involves the cyanoethylene group, which is derived from the monomer acrylonitrile. If this group alone is present in (a₂), then its quantity should not fall below 0.1, preferably 1 and in particular 5 % by weight of (a₂). If some other groups (a₂₂), (a₂₃) and/or (a₂₄) are used apart from this group, then their quantity is 0.1 to 8 % by weight. Regardless of whether (a₂₁) is used alone or together with other groups (a₂₂), (a₂₃) and/or (a₂₄), the content of this group in (a₂) should not exceed 8 % by weight, because otherwise the danger of the blend of (a₂) and PPE separating exists.

In the case of the group (a₂₂) it involves the 1-methyl-1-phenylethylene group, which is derived from the monomer α -methylstyrene. If this group is present alone in (a₂), then its quantity should not fall below 1 % by weight, preferably 2 % by weight and in particular 4 % by weight of (a₂) and not exceed 60 % by weight of (a₂). It is found, that a (a₂₂) quantity of 1 to 30 in (a₂), preferably 1 to 10 and in particular 3 to 8 % by weight is particularly advantageous here. If this group is used together with other group(s) (a₂₁), (a₂₃) and/or (a₂₄), then its content in (a₂) decreases by the quantity of the other groups (a₂₁), (a₂₃) and/or (a₂₄) present in (a₂), provided the total quantity of the groups (a₂₁) to

(a₂₄) reaches 60 % by weight of (a₂). It is advantageous here, if the weight ratio of (a₂₂) to the groups (a₂₁) and/or (a₂₄) is greater than 1, when these are also used.

In the case of the group (a₂₃) it involves the 4'-methylphenylethylene group, which is derived from the monomer p-methylstyrene. If this group is present alone in (a₂), then its quantity should not fall below 1 % by weight, preferably 2 % by weight and in particular 4 % by weight, of (a₂) and not exceed 80 % by weight of (a₂). It is found, that a (a₂₃) quantity of 1 to 30 % by weight in (a₂), preferably 1 to 10 % by weight and in particular 3 to 6 % by weight, is particularly advantageous here. If this group is used together with other groups (a₂₁), (a₂₂) and/or (a₂₄), then its content in (a₂) also decreases by the quantity of the other groups (a₂₁), (a₂₂) and/or (a₂₄) present in (a₂), provided the total quantity of the groups (a₂₃), (a₂₁), (a₂₂) and/or (a₂₄) reaches 60 % by weight of (a₂). It is however very much advantageous to use the group (a₂₃) and the group (a₂₂) together. Here the weight ratio of (a₂₃) to (a₂₂) can widely vary, with the proviso, that (a₂₂) or (a₂₃) quantity in the part (a₂) is not reduced below 1 % by weight by this at any time.

In the case of the group (a₂₄) it involves groups of the general formula (1), which are derived from acrylates or methacrylates. Examples of largely suitable groups (a₂₄) are the 1-carboxymethyl-, -ethyl-, -propyl-, -isopropyl-, -n-butyl-, -tert-butyl-, -amyl-, -hexyl-, heptyl-, -octyl-, -2'-ethylhexyl-, -nonyl-, -decyl-, -cyclopentyl-, -cyclohexyl-, -2'-methylcyclohexyl-, -2',4'-dimethylcyclohexyl-, -phenyl-, -4'-methylphenyl- or 1-carboxynaphthylethylene groups or the corresponding 1-methylethylene groups. These largely suitable groups are derived from the methyl-, ethyl-, propyl-, isopropyl-, n-butyl-, sec-butyl-, tert-butyl-, amyl-, hexyl-, heptyl-, octyl-, 2'-ethylhexyl-, nonyl-, decyl-, cyclopentyl-, cyclohexyl-, 2'-methylcyclohexyl-, 2,4 -dimethylcyclohexyl-, phenyl-, 4'-

methylphenyl- or the naphthyl ester of the acrylic acid or methacrylic acid. Here the groups (a_{24}), which are derived from the methacrylates, are particularly preferred, of which again the 1-carboxy-2'-ethylhexyl-, the 1-carboxyphenyl- and the 1-carboxy-4'-methylphenyl-1-methylethylene groups are most preferred. These can be used individually or together.

If groups (a_{24}) are present alone in (a_2), then their quantity should not fall below 0.01 % by weight, preferably 1 % by weight and in particular 4 % by weight of (a_2) and not exceed 10 % by weight of (a_2). It is particularly advantageous if the groups (a_{24}) are not used alone but used together with the other groups (a_{21}), (a_{22}) and/or (a_{23}). Here the weight ratio of (a_{24}) to these other groups is in the range of 0.01 to 1, and in particular 0.2 to 1. In this common use of the group (a_{24}) with the other groups (a_{21}), (a_{22}) and/or (a_{23}), its content in (a_2) should not exceed the maximum limit of 10 % by weight of (a_2) decisive for its individual application and not fall below the decisive lower limit of 0.01 % by weight of (a_2).

According to the present invention, the groups (a_{21}), (a_{22}), (a_{23}) and/or (a_{24}) can be present in the part (a_2) of the blend of PPE and (a_2) forming the substrate (a) as randomly distributed monomer units in the polymer main chains of styrene copolymers. Here it involves random copolymers of styrene and the corresponding monomers, as they are known as such and can be prepared by radical copolymerisation. These random copolymers have, in general, a number average molecular weight \bar{M}_n of 2×10^3 to 3×10^5 . The copolymers must have the compositions to be used according to the present invention as indicated above. Examples of particularly advantageous random copolymers are copolymers produced by radical copolymerisation of

- 93 parts by weight of styrene and 7 parts by weight of acrylonitrile;
- 95 parts by weight of styrene, 3 parts by weight of acrylonitrile, 1 part by weight of 2-ethylhexyl methacrylate and 1 part by weight of phenyl methacrylate;
- 70 parts by weight of styrene and 30 parts by weight of α -methylstyrene;
- 70 parts by weight of styrene and 30 parts by weight of p-methylstyrene;
- 60 parts by weight of styrene, 15 parts by weight of methylstyrene and 25 parts by weight of p-methylstyrene;

or

- 50 parts by weight of styrene, 45 parts by weight of methylstyrene, 3 parts by weight of acrylonitrile and 2 parts by weight of 4'-methylphenyl methacrylate, of which the styrene- α -methylstyrene, styrene-p-methylstyrene and the styrene- α -methylstyrene-p-methylstyrene copolymers are most preferred.

According to the present invention the groups (a_{21}), (a_{22}), (a_{23}) and/or (a_{24}) can be present in the part (a_2) of the blend of PPE and (a_2) forming the substrate (a) but also in the form of homogeneous oligimeric or polymeric blocks of (a_{21}), (a_{22}), (a_{23}) and/or (a_{24}). These blocks can be incorporated as component of styrene copolymers in the polymer

main chains of the styrene polymers and/or bonded as side radicals to the polymer main chains of the styrene polymers. In this case it also includes graft or block copolymers of the styrene with acrylonitrile, α -methylstyrene, p-methylstyrene and/or the above mentioned (meth)acrylates. Such graft and block copolymers are known as such and can be produced according to conventional procedures. The exact type of the bonding of the used blocks between each other can be varied as desired, provided the block and graft copolymers have the total compositions as indicated above to be used, according to the present invention. If these compositions are beyond the critical limits, then the relevant block or graft copolymers - irrespective of a special type of the block bonding present in certain cases - are unsuitable for the formation of the substrate (a) to be used according to the present invention.

According to the present invention it is however particularly advantageous, if in the part (a₂) of the blend of PPE and (a₂) forming the substrate (a) the groups (a₂₁), (a₂₂), (a₂₃) and/or (a₂₄) form the monomer units of oligimeric or polymeric homopolymers, copolymers or Block or graft copolymers, which are produced separately and subsequently mixed with polystyrene in such a quantity, that the composition of the part (a₂) resulting in this manner is within the critical limits as indicated above. In this case the blend forming the substrate (a) consists of PPE, polystyrene, at least one homopolymer or copolymer of the groups (a₂₁), (a₂₂), (a₂₃) and/or (a₂₄) as well as in certain cases additional additives. The polystyrene normally has a weight average molecular weight \bar{M}_w of more than 8×10^4 , in particular in the range of 1×10^5 to 2×10^5 . Here it is quite advantageous, to use the groups (a₂₂) and (a₂₃) together. These groups preferably form the monomer units of oligomeric α -methylstyrene-p-methylstyrene-

copolymers, which can be produced in a known method by radical copolymerization in the absence of solvent or in solution and then added to the polystyrene in required quantity according to the present invention. The copolymers of this type most preferred according to the present invention have a number average molecular weight \bar{M}_n of 5×10^3 to 1.5×10^4 . In general they have a weight average molecular weight \bar{M}_w of 5×10^3 to 3×10^4 , preferably of 6×10^3 to 2.5×10^4 and in particular of 7×10^3 to 2×10^4 . In general these copolymers, based on their respective quantity, consist of 1 to 99 % by weight, in particular 2 to 98 % by weight, of 1-methyl-1-phenylethylene groups (a_{22}) and 99 to 1 % by weight, in particular 98 to 2 % by weight, of 4'-methylphenylethylene groups (a_{23}). These copolymers are added to the polystyrene in a quantity, based on (a_2), of 1 to 30 % by weight, preferably 4 to 23 % by weight and in particular 4 to 5 % by weight, wherein additional quantities of these copolymers to the polystyrene in the range of approximately 7.5 to about 16 % by weight, based on (a_2) have also proved as extremely favourable and advantageous. Here it is to be taken care, that the above % by weight, based on (a_2), does not fall below the lower limit of 1 decisive for the individual use of the groups (a_{22}) and (a_{23}), what however can be avoided easily, by selecting properly formed copolymers. It has been found however, that these lower limits decisive for the individual use of the groups (a_{22}) and (a_{23}) in the case of the above described, particularly preferred execution form of the invention, according to which the part (a_2) of the blend forming the substrate (a) consists of a mixture of polystyrene and the above described low molecular weight α -methylstyrene-p-methylstyrene-copolymers, containing in certain cases additives, are not so critical, so that in this case it is also possible to deviate from them, i.e., it is possible to fall below one of these lower limits for (a_{22}) or (a_{23}) without any serious disadvantages.

Further the part (a₂) of the blend of PPE and (a₂) forming the substrate (a) may have compatible additives, wherein by the term "compatible" it is meant, that these additives get distributed in the blend without causing opacity and also do not cause any opacity under the influence of laser light in the course of time. These additives should therefore be distributed in the blend in molecular disperse form. Moreover they should absorb light of wavelength λ in the range of 720 to 1000 nm only weakly or should not absorb at all. In general it may involve antioxidants, lubricants, plasticisers and dyes as the above additives. Examples of suitable additives are tert.-butylcresol, white oil and zinc stearate. The additives may be added in a quantity of up to 10 % by weight, based on (a₂), where care is to be taken, that by this the polystyrene content or the content of phenylethylene groups (a₂₅) in (a₂) does not fall below 40 % by weight.

A very particularly preferred substrate (a) of the invention-related sheet-like, multilayer, laser-optical recording material has concentric or spiral tracks or other suitable structures for the guidance of the laser beams in one of its surfaces (a₁) and consists of a blend of, based on the blend,

34 to 40 % by weight of PPE and

60 to 66 % by weight of the part (a₂),

wherein the part (a₂) of this blend, based on (a₂), consists of

68.7 to 96.889 % by weight of polystyrene of a weight average molecular weight \bar{M}_w of above 8×10^4 ,

3 to 25 % by weight of a random copolymer of, based on its quantity, 2 to 98 % by weight of copolymerized α -methylstyrene and 98 to 2 % by weight of copolymerized p-methylstyrene with a weight average molecular weight \bar{M}_w of 7×10^3 to 2×10^4 ,

0.1 to 6 % by weight of a plasticiser, for example, white oil,

0.01 to 0.1 % by weight of an antioxidant, for example, tert.-butylcresol, and

0.001 to 0.2 % by weight of a dye, which absorbs light of wavelength $\lambda > 720$ nm only weakly or does not absorb at all.

The further essential component of the invention-related, sheet-like, multilayer, laser-optical recording material is its amorphous, thermally modifiable recording layer (b). Here it includes the conventionally known recording layers, as they are usually used for the laser-optical data recording according to the principles described at the beginning. In general the recording layer (b) is 10 to 500 nm thick.

Moreover, the invention-related recording materials may contain further layers that can also be important for the functioning of the recording materials, such as somewhat conventionally known reflector layers, antireflection layers or adhesive layers or layers, which decompose on heating and form gases. In addition the recording layers (b) may also be covered with optically transparent protective layers, which prevent the dirt particles or scratches in the laser focus or prevent corrosion of the layers (b). In general conventionally known polymers or silica are used for this. For this purpose the recording material, according to the present invention, may also be joined with an optically transparent cover in a conventional manner, such as ultrasonic welding.

Two recording materials, according to the present invention, can also be so joined in pairs with each other, so that their recording layers face each other in parallel and there is a certain distance between them. This distance can be adjusted in a conventionally known manner with the help of spacers, like webs or small columns. An individual invention-related recording material can also have two recording layers on the sides of a substrate (a) facing one another.

The preparation of the recording material related to the invention can be done according to conventional present-day technology. In general, this is done by the forming process of the blend forming the substrate (a) with the help of the injection moulding technique. The structured surface (a₁) of the substrate (a) is formed usually and effectively by injection moulding of the substrate (a) into the desired form. After the injection moulding of the substrate (a) (process step I) the respective recording layer (b) is applied, in certain cases after the application of intermediate layers, reflector layers, among other things, on the structured surface(s) (a₁) of the respective substrate (a) by

vapour deposition, sputtering or by solution coating (process step II). Afterwards further layers, which are helpful for the functioning of the recording material, can be applied on the respective recording layer (b). Subsequently, the recording material may be provided with a cover.

The blend of PPE and the part (a₂) to be used, according to the present invention, forming the substrate (a) can be in principle produced with the help of any conventionally known mixing techniques. In the scope of the present invention it has however proved to be particularly advantageous to prepare the blend by co-extrusion of its components using a twin screw devolatilisation extruder. In this process, the part (a₂) of the blend is melted in the extruder and the PPE is metered continuously into the melt as a highly concentrated, preferably 10 to 80 % solution in toluene or ethyl benzene. The components are homogeneously mixed with each other in the extruder at temperatures of 200 to 400 °C, wherein the solvent is continuously distilled off. The PPE can however be fed into the extruder even in solid form, for example as granules. The resulting blend is removed from the extruder under clean room conditions, granulated and fed into the injection-moulding machine. The blend can also be fed directly into the injection-moulding machine.

Analog or digital data can be recorded on the invention-related recording materials by means of a write laser beam - an analog modulated continuous-wave laser for writing analog data and a pulse-modulated laser for writing digital data.

In general, suitable lasers have an (beam) output of 1 to 20 mW at the recording wavelength λ . The focus diameter of the write laser beam is generally 300 to 2000 nm. Usually, the pulse duration during the exposure with a pulse-modulated laser is 10 to

1,000 ns. For writing, a laser beam of light of wavelength λ is used advantageously, which is absorbed well by the relevant recording layer (b). Wavelengths λ of 400 to 1000 nm are advisable.

During the write operation, the laser beam is moved over the recording material relatively and impinges on the latter at right angles or obliquely. In the case of perpendicular impingement it can be focused on the recording layer (b), whereas in the case of oblique impingement it must be focused. At the point of impingement the recording layer (b) is locally heated and thermally modified regions result there, for example, in the form of holes, pits, spots, relief structures or magnetically reversed regions. During the writing of data with pulse-modulated laser beams, these regions have essentially a circular or oval base area with a diameter of 100 to 2,000 nm, whereas during writing with an analog modulated continuous-wave laser they may have any base area form.

The invention-related recording materials are suitable mostly for all known types of laser-optical data recording. In particular, they are suitable for magneto-optical data recording.

Writing of data in the recording layer (b) is possible from the side of the layer facing away from the substrate (a) or through the optically transparent substrate (a). The latter method is particularly advantageous.

The recorded data is read with the help of a read laser beam. The (beam) output of the read laser at the read wavelength λ' is below the threshold power, above which recording is possible. In general, the (beam) output is 0.1 to 2 mW. Laser light of

wavelength λ' , which is reflected by the recording layer strongly, is used advantageously. Wavelengths λ' of 400 to 1000 nm, in particular 630 to 900 nm, are advisable.

During the reading process also, the read laser beam is moved over the recording material relatively and impinges on the latter at right angles or obliquely. In the case of perpendicular impingement it can be focused on the recording layer (b), whereas in the case of oblique impingement it must be focused on it.

If the read laser beam impinges on a thermally-modified region while moving over the recording layer (b), then the properties of the light transmitted or reflected by the recording material change and the change can be detected with the help of suitable detectors.

Here, the reading of data in the recording layer (b) can be done from the side of the layer (b) facing away from the substrate (a) or through the substrate (a), where the latter method is advantageous. It is particularly advantageous to collect the reflected light.

In addition, it is particularly advantageous here to use write laser and read laser, which emit laser light in the infrared wavelength range of 630 to 900 nm. Here, it is also advantageous if the recording wavelength λ is identical to the read wavelength λ' or differs only slightly from it. Light of these wavelengths is provided by conventional semiconductor-lasers.

Data is thus written on the invention-related recording materials in a preferred process according to the present invention through the substrate (a) using pulse-modulated laser light of wavelength λ of 630 to 900 nm, in particular 740 to 850 nm.

Afterwards the data is read from the described recording materials in a preferred process according to the present invention with laser light of wavelength λ' , of 630 to 900

nm, in particular 740 to 850 nm from the side of the substrate (a), wherein the light reflected by the recording layer (b) is collected.

If the invention-related recording materials are present as data disks, then the conventional, known disk drives can be used for writing and reading digital data.

The invention-related recording materials have numerous special advantages.

Also they can be produced in a simple manner and their property profile can be reproduced very easily and reliably.

Due to the special advantageous properties of the blend forming the substrate (a), the substrates (a) can be injection-moulded under particular low-stress conditions. It results in excellent shaping of the tracks that have a consistently good profile over the entire surface of the substrate (a). After their preparation, the substrates (a) have no thermal distortion and have considerably reduced internal stress. Moreover the PPE content in the blend can be reduced below the level known from state-of-the-art technology and the substrate (a) produced from this does not exhibit birefringence. The reduction of the PPE content in the blend, relatively difficult to be processed, leads to an easier and more exact injection moulding process apart from cost reduction. The corresponding substrates (a) always have outstanding resistance to heat distortion and dimensional stability, a high modulus of elasticity and a high hardness as well as extremely low water absorption. Moreover, they absorb light of a wavelength λ of above 600 nm to a very small extent or no more at all, so that they are especially suitable for the generally preferred writing and reading of the data through the substrate (a). Moreover the substrates (a) are also very suitable for the preparation of audio or video compact disks. Apart from the aforesaid laser-optical recording materials with amorphous,

thermally modifiable recording layer (b), the objects of the invention are also audio or video compact disks, which have an invention-related substrate (a) of the above described type. In the case of the compact disks, the data is not written by means of laser beams in the form of thermally modified regions on a recording layer, but transferred onto the disk in a known manner by the mastering-process, i.e., pressed into the substrate (a) of the disk.

The tracking behaviour of the invention-related recording materials is excellent, i.e., the tracking servo systems and auto-focusing means of the conventional, known disk drives function in a very exact manner in the case of the invention-related recording materials. The tracking servo systems and auto-focusing means are compatible with the invention-related recording materials even better than with those recording materials that merely contain the known substrates.

Totally, the invention-related recording materials have increased life, can be used for recording with comparatively low laser power and have a signal-noise-ratio of more than 45 dB. Due to their particularly high bit density and pronounced low bit error rate, the recording materials are very much suitable for recording video signals. Moreover they are suitable as archive data disks.

Examples and comparative experiments

In the following examples and comparative experiments the thickness of the individual layers was determined by scanning electron micrograph recordings.

The signal-to-noise ratio was evaluated in a known manner for recording materials that had been written on with the help of pulse-modulated laser (wavelength λ of the emitted light: 830 nm; pulse duration 500 ns; light output: 6 mW) through the substrate (a). For this purpose, the recording materials were read through the substrate (a) with the help of a continuous-wave laser (wavelength λ of the emitted light: 780 nm; light output: 0.5 mW). The emitted read laser beam was always moved over the recording layers with a relative speed of 4 m/s. Then the light reflected by the recording materials was continuously collected and analysed.

In the following examples and comparative experiments, substrates (a) were used, which contained concentric tracks on their surface. The tracks serve for the exact guidance of the write and read laser beams, which are emitted by the laser-optical write and read head of the disk drive. For this purpose, it is necessary that the track positioning servo systems available in the laser-optical head receive sharp optical signals. These signals result from diffraction of the laser light reflected by the recording material to the laser-optical head at the boundary between the groove and land and for the collection and analysis of these light signals the conventional, known photodiode arrangements are used. For the tracking behaviour, i.e., the exact guidance, in particular of the read laser beams, it is essential, that high optical contrast should exist between land and groove, otherwise only weak and scattered or no signals are received. The latter is often the case

in respect of the described recording materials. This however leads to a low signal-to-noise ratio and hinders the recovery of written data. In general therefore, as a measure of the quality of tracking, the width of the signals as well as the difference in intensity of the laser light reflected by a groove and by a land are taken. Another criterion of quality is whether this intensity difference is constant and high over the entire diameter of the recording material.

Accordingly, the tracking behaviour of the recording materials was evaluated such as below by the reading of the materials with a read laser beam ($\lambda = 780, \text{ nm}$; light output: 0.5 mW) transverse to the tracks. Measurement was done over the entire diameter of the recording material. The reflected laser light was collected with the help of conventional, known optical arrangements, sent to photodiodes and converted into electrical signals by suitable electronic components, whose magnitude was plotted as function of the diameter. An evaluation was made to ascertain if the differences between the magnitude of the signals received by the lands and that received by the grooves over the entire diameter of the recording material were consistently sharp and high. The following rating of the tracking behaviour was made, based on the evaluation:

Very good: sharp signals; large difference between the magnitudes of the land - and groove signals, which is constant over the entire diameter;

Good: sharp signals; small difference between the relevant signal levels, which varies over the entire diameter more or less strongly;

Unsatisfactory: wide, diffused signals; small difference between the relevant signal levels; in certain cases this difference varies over the entire diameter more or less strongly;

Poor: no difference between the relevant signal levels.

In order to check if the recording on the recording materials caused a change in their tracking behaviour, both the unrecorded as well as the recorded recording materials were measured and rated in the manner indicated above. If serious differences were produced in the tracking quality of a recording material in the unrecorded condition on the one hand and in the recorded condition on the other hand, then this presented a serious disadvantage. If this quality difference, starting from a high level, was low, then this verified the particular advantage of the relevant recording material.

The Melt Flow Index (MFI) of the produced blends, the reflectivity (%) and the recording sensitivity (nJ) of the recording layers (b) as well as the birefringence of the substrates (a) were evaluated with the help of conventional, known measurement methods.

Examples 1 to 2 and comparative experiment 1

Preparation and properties of the substrates (a) to be used according to the present invention (examples 1 and 2) and of a known substrate (comparative experiment 1);

Blends were produced under exactly comparable conditions, in which the poly-(2,6-dimethylphenylene ether)-content (PPE) according to the patent US-A-4 373 065 was not sufficient, to compensate for the orientation birefringence of the blends completely. The blends had the following composition:

Comparative experiment 1

32.5 kg of radically polymerised polystyrene with a weight average molecular weight \bar{M}_w of 1.65×10^5 and
17.5 kg of poly-(2,6-dimethylphenylene ether) (PPE);

Example 1

30.0 kg of polystyrene as in the comparative experiment 1,
2.5 kg of a copolymer from α -methylstyrene (10 % by weight) and p-methylstyrene (90 % by weight) with a weight average molecular weight \bar{M}_w of 9×10^3 and
17.5 kg of PPE as in the comparative experiment 1;

Example 2

27.5 kg of polystyrene as in the comparative experiment 1,
5.0 kg of a copolymer as in example 1 and
17.5 kg of PPE as in comparative experiment 1.

The part (a₂) of the blends (comparative experiment 1: polystyrene; examples 1 and 2: polystyrene plus copolymer) was melted in a twin-screw devolatilisation extruder, and the PPE was metered into the respective melt as 60 % solution in toluene.

The blends were homogenised in the twin-screw extruder by devolatilisation at 280° C and a dwell time of one minute, taken out from the extruder under clean-room conditions and converted into granules.

The granules pre-dried at 110°C were injection-moulded in clean-room conditions in a 90-tonne injection-moulding machine and a special mould for optical storage disks to get disks [substrate (a), examples 1 and 2; known substrate, comparative experiment 1]. Here concentric tracks were pressed into one side of the substrate by means of a nickel die inserted into the mould. The substrates were 1.2 mm thick and had a diameter of 130 mm; the pressed tracks were 70 nm deep and 0.6 µm wide (groove) with a distance of 1.6 µm (land).

The injection moulding parameters were set for each of the three blends and the planarity of the substrate and minimum birefringence between crossed polarisation filters were optimised. The results are found in table 1.

Table 1

Injection moulding parameters of the blends and property profile of the substrates produced from them			
Injection moulding parameters and property profile of the substrates	Comp. Exp. 1	Example 1	Example 2

Melt Flow Index MFI such as per DIN 53 735 of the blends at 300°C and a applied force of 5 kp	(g/10 min)	66	81	97
Injection speed of the blends	(mm/sec)	90	100	120
Optimum injection temperature for the blends	(° C)	350	340	330
Colour of the substrates		yellow	yellow	light
Maximum birefringence of the disks in the radius range 25 to 60 mm	(nm)	15	2	2
Track-shaping on the substrates		good	very good	very good
Planarity of the substrates		good	very good	very good
Maximum temperature of the substrates in continuous use	(° C)	125	125	125

As the comparison shows, in the case of the invention-related substrates (a) of examples 1 and 2 many improvements have taken place with respect to those of the comparative experiment 1: The reduction of the melt viscosity led to the reduction of the injection temperature and to decreased thermal damage of the blends. Furthermore, the shaping of the mould was clearly improved without reducing the maximum temperature in continuous use. The drastic decrease of the orientation birefringence to almost no more measurable values is to be particularly emphasised. Accordingly, the invention-related substrates (a) (examples 1 and 2) are clearly superior to the known substrate (comparative experiment 1).

Examples 3 to 4 and comparative experiment 2

Preparation and properties of invention-related recording materials (examples 3 and 4) and of a known recording materials (comparative experiment 2);

Two of the substrates (a) of the examples 1 and 2 (for the examples 3 and 4) as well as two known substrates of the comparative experiment 1 (for the comparative experiment 2) were each coated in a spin-coating unit at 3000 rpm with a propanolic solution (4 % by weight) of a mixture of a dye absorbing at $\lambda = 700$ to 850 nm and a solution polymer of methyl Methacrylat and methacrylic acid. The weight ratio of dye to polymer was 70:30. A triquinocyclopropane dye was used as dye. After drying, recording materials with approx. 100 nm thick recording layers (b) were obtained, whose reflectivity for light of wavelength $\lambda = 780$ nm was determined as 19 % (measurement in known manner through the substrate).

Two identical recording materials were each glued with the dye layers in the form of inward sandwich, where a ring of 300 μm thick was laid in between as spacer.

Digital data were written in the grooves of the recording materials on a disk drive. Subsequently the data was read.

The results obtained in this case have been given in table 2.

Table 2

Laser-optical data recording with invention-related and non-invention-related recording materials			
Parameter	Comparative experiment 2 ^a	Example 3 ^b	Example 4 ^c
Recording sensitivity	1-2 nJ	1-2 nJ	1-2 nJ
Read signal	good	good	good
Tracking behaviour of the unrecorded recording material	good	very good	very good
Tracking behaviour of the recording material with recorded information	unsatisfactory	good	good

a) Substrate of the comparative experiment 1

b) Substrate (a) of the example 1

c) Substrate (a) of the example 2

The results can be summarised as follows:

While the performance characteristics that relates to the dye layer, such as recording sensitivity and read signal, were not affected by the different substrates, a clear improvement of the tracking could be observed in the case of the invention-related recording materials (examples 3 and 4). The very densely recorded parts of the known recording material could hardly be read, whereas in the case of the invention-related recording materials tracking was easy.

Example 5

Preparation and properties of invention-related recording material with a recording layer (b) of tellurium:

On one side of a substrate (a) prepared according to example 1, tellurium was vapour-deposited to a layer thickness of 50 nm in a vacuum apparatus.

On a disk drive, digital data was written in the grooves and subsequently read. The signal-to-noise ratio was 52 dB.

Example 6

Preparation and properties of an invention-related magneto-optical recording material:

On several substrates (a) prepared according to example 1, a 90 nm thick AlN layer was sputtered in a high vacuum apparatus. Subsequently in vacuum a blend of the composition with 2 parts by weight of Nd, 18 parts by weight of Dy, 95 parts by weight of Tb and 30 parts by weight of Co was applied to a layer of 75 nm thickness. For the protection of the magneto-optical recording layer, a 50 nm thick SiO_x-layer was vapour-deposited on this. On a disk drive, digital data was written in the recording layer and read magneto-optically. The signal-to-noise ratio was 50 dB throughout.

Comparative experiment 3

Preparation and properties of a magneto-optical recording material with a known substrate:

Example 6 was repeated with the difference that substrates of the comparative experiment 1 were used instead of the substrates (a) to be used according to the present invention.

The recording materials thus obtained showed a signal-to-noise ratio of below 45 dB.

Example 7

Preparation and properties of an audio compact disk with a substrate (a) to be used as per the present invention:

Audio compact disks were prepared from the blend described in example 1. For that purpose the granules were pre-dried and injection-moulded with the same injection-moulding machine but with another mould with a compact disk die. The obtained substrates (a) had a diameter of 100 mm and were free of birefringence.

The light yellow substrates (a) were coated by vapour deposition in vacuum with a thin aluminium layer and covered with a protective lacquer. The compact disks were

played using commercial equipment; no differences could be established with regard to the reproduction quality compared with the conventional polycarbonate disks.